

Efficient grafting of redox-active ferrocene polymers from α,ω -diiodoalkanes at cathodically charged glassy carbon

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Abstract α,ω -Dihaloalkanes, when cathodically reduced at glassy carbon (GC), can be immobilized at the electrode surface. The present contribution focuses on the reduction of 1,8-diiodooctane, as model dihalo-substrate, in an aprotic organic solvent containing tetraalkylammonium salts as electrolyte. It is expected that these compounds in contact with GC, polarized at potentials more negative than -1.7 V versus Ag/AgCl, partly lead to monoiodoalkyl chain immobilization onto carbon. The process corresponds to the cathodic charge of graphitized and fullerenized zones present in carbon followed by a displacement reaction (analogous to a nucleophilic attack) towards pending C–I functions. This mode of grafting is then applied to the reaction of negatively charged carbon with bis-(ω -iodoalkyl)ferrocenes. Ferrocene is then used as an efficient redox probe. This study aims to point out the formation of a chemically grafted redox polymer at carbon electrodes that permits one to quantify the level of immobilized alkyl chains according to their chain length. Coverage levels were found to be high, and surface concentrations of ferrocene currently $>10^{-8}$ mol cm $^{-2}$ were reached. Ferrocene layers deposited onto carbon were found to be chemically and electrochemically stable and expected to be suitable for efficient electricity storage.

Keywords α,ω -Dihaloalkanes · Cathodic cleavage · Carbon surface modification · Ferrocene immobilization

1 Introduction

Glassy carbon (GC) is known to be a convenient electrode material to carry out analyses and electrolyses both within cathodic and anodic range; however, a particular interest of this article concerns its use as a cathode. GC has been considered for a long period as a typical ‘inert’ material made of sp^3 carbon atoms without any specific reactivity [1]. Such an ideal structure does not look suited to the recent development of modified carbon surfaces by means of chemical or electrochemical reduction of diazonium salts [2] involving intermediary free aryl radicals. This way of formation of the covalent bonds obviously implies the presence of unsaturated systems in the material matrix. Quite recent studies have stressed that GC (industrially prepared by carbonization of phenolic resins [3]) presents a structure which is somewhat complex. It is now known that GC contains sheets or ribbons of graphite-like structures in discontinuity with ‘crystallite’ boundaries expected to represent all types of carbons prepared in such a way. In other words, GC contains a large proportion of sp^2 carbon atoms belonging to nanometric graphitized areas [4, 5] formed under pyrolysis at high temperatures (up to 2,500 °C). It then appears quite certain that a tight mixture of sp^2 and sp^3 carbon zones may co-exist in the bulk and at the polished surface. Actually, graphite particles together with parent graphenes and fullerenes may co-exist in the material with ‘polyaromatic materials’ made of graphitic particles [6]. Therefore, given its intrinsic partial unsaturation, GC surface could be seen as a cathodically active material when quite negative potentials are reached, especially when aprotic solvents are considered.

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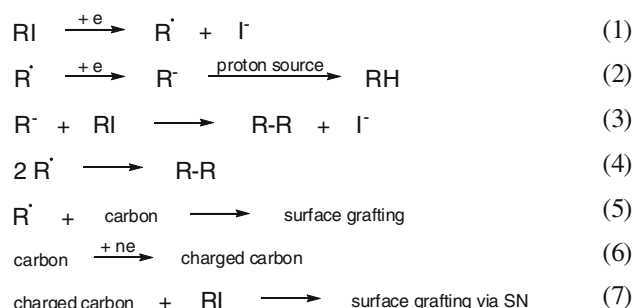
Therefore, one must consider GC as an electronic conductor chemically modified, at least at its surface, by reactive π acceptor microzones. Thus, in aprotic organic solvents in the presence of electrolytes M^+X^- , the polarization of GC at less than -1.7 V versus Ag/AgCl yields superficial nucleophilic species reactive enough to modify interfacial processes to a large extent. As already reported, highly oriented pyrolytic graphite (HOPG) leads under cathodic charge [7] to well-defined insertion stages $[C_n^-, M^+]$ and the material turns to resemble a ‘carbon amalgam’ stable in the absence of air and being an efficient reducing agent (especially in the case where n is small). In the meantime, it was reported that concomitant insertion of electrons and cations into HOPG produces a nucleophilic material [8] capable of reacting with a large panel of electrophilic species. Especially, the contact of charged HOPG with CO_2 permits the formation of a graphite polycarboxylate [9]. Alkyl bromides were also reported to react similarly (graphite alkylation [10]). Two concomitant processes such as *charge* (in mass) and *reduction* (at surface) of electron-acceptors present in GC should be taken into account in order to explain the reactivity of graphite. The exact nature of interface reactions [electron transfer(s) vs SN displacement(s)] is worth being re-considered.

More specifically, alkyl halides RX belong to a peculiar series of electrophilic species; many studies in the field of electrochemical synthesis and analysis concern these species [11]. It is well known (Scheme 1) that 1-iodoalkanes RIs are electrochemically reduced at GC following a two-electron bond cleavage process with the major formation of the corresponding alkane RH [12, 13]. Quite generally, the two-electron character of this process is due to a large cathodic activation and to the instability of the free radical R^\bullet [arising from dissociative electron transfer according to reaction (1) and reduced at a potential less negative than that required for the two-electron bond scission, Eq. (2)]. In aprotic organic solvents, some amounts of homodimers could be formed either by homocoupling (reaction 4), or—more likely—obtained in a Wurtz process (reaction 3) implying organic carbanions which may act as nucleophilic transients.

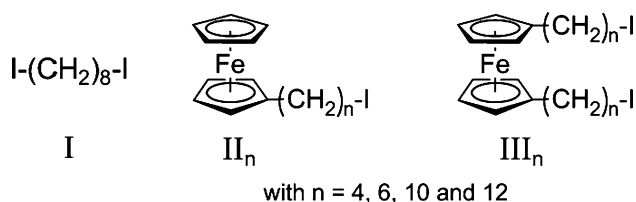
It is also of interest that charging of GC may happen in the meantime which provokes indirectly a surface reaction not via a free R^\bullet radical but by means of nucleophilic substitution as shown by Eqs. (6, 7) owing to a possible charge of carbon.

As a matter of fact, such reactions require quite negative potentials ($E \ll -1.5$ V) that render unlikely the grafting of n -alkyl chains onto carbon via a free radical reaction.¹

¹ The reduction of RIs corresponds to a two-electron cathodic scission with a free alkyl radical as transient. Estimations concerning the standard potentials for the reduction of R^\bullet were reported [14].



Scheme 1 Reduction of alkyl iodides



Scheme 2 Diiodo derivatives studied

Interestingly, cathodic voltammetric experiments achieved with 1-iodohexane showed a progressive inhibition of the electrode [15], but definite evidence concerning the exact nature of the organic deposit onto the GC surface was brought by using ω -iodoalkyl-ferrocenes (II) [16]. Such a process, already mentioned for primary and secondary alkanes [17, 18], can also be considered as an efficient method of immobilization of π donors such as tetra-thiafulvalene derivatives [19], specifically by means of covalent carbon–carbon bonds.

It is therefore proposed here to reconsider, at GC electrodes, the reduction of α,ω -diiodoalkanes [with 1,8-diiodooctane (I) chosen as a model substrate] for comparing the electrode behaviour of α,ω -diiodoalkanes (III) with a ferrocene moiety incorporated into their aliphatic backbone (seen under a widest scope) in aprotic polar solvents with a special focus on researching evidences of surface modifications of GC and graphite (Scheme 2). The building of compact films from primary RIs has been already described and discussed as a function of the chain length. Quantification of surface deposits is worth being considered by means of ferrocene moieties. On the other hand, ω -iodoalkylferrocenes used as a probe showed that ferrocene was directly immobilized in large amounts onto carbon [16]. As redox polymers labelled with ferrocene are expected to be generated by Wurtz coupling in basic media, the influence of linker length in C_n and the anodic response of different ferrocene moieties (directly fixed to carbon or belonging to the polymeric bulk) appeared worthy of study and comment. Then, a better knowledge of redox layers (partially immobilized) at a GC surface could be obtained and the formation of high-density coverages allows

considering this method as very promising for deposition of specific functions.

The described method presented hereafter could thus be perceived as a new recipe for building modified carbon surfaces for catalysis, analysis and other specific applications.

2 Experimental section

2.1 Chemicals

Carbon materials were purchased from Tokai Carbon C° (code: GC Rod, for building GC stationary electrodes) and from Carbone-Lorraine (large plates, code: VD 1500 and 2500, thickness 3 mm).

Aliphatic iodides (RI) and ferrocene (Aldrich), and α,ω -dihaloalkanes (Acros), all of purity >98 %, were used without further purification. The redox probes used in the present contribution (series II and III) were prepared according to the following general procedures.

ω -Haloalkylferrocenes were synthesized using a method inspired from [19]. For this, 4.7 mL (6.6 mmol, 1.1 eq.) of a 1.4 M solution of *t*-BuLi in pentane was added dropwise to the solution of ferrocene (1 g, 5.5 mmol, 1 eq.) in THF (18 dm³) at 0 °C and the obtained mixture was additionally stirred for 40 min. The corresponding bromochloroalkane Br(CH₂)_nCl (7.2 mmol, 1.2 eq., neat or in 10 dm³ of THF, if solid) was then added and the solution was stirred for 3 h. The reaction mixture was quenched with a saturated aqueous solution of NaCl and extracted with diethyl ether. The organic layer was dried over Na₂SO₄, the solvent stripped on a rotary evaporator and the crude product was separated by chromatography on a SiO₂ column (hexane). Thus, obtained Fc(CH₂)_nCl was refluxed overnight with a fivefold excess of KI in dry acetone. After KCl was filtered off through a Celite filter, the solvent was evaporated to give ω -iodoalkylferrocene (quantitative conversion).

Bis(ω -iodoalkyl)ferrocenes (III) were prepared by the above method using 1:2 ferrocene-to-butyllithium ratio and 2.6 eq. of the corresponding α,ω -dihaloalkane; before conversion into the parent iodides, intermediate Cl and Br derivatives were separated by chromatography on a SiO₂ column.

NMR spectra were acquired with a Bruker 300 MHz spectrometer (in CDCl₃ using TMS as internal standard).

2.1.1 4-Iodobutylferrocene, Fc(CH₂)₄I, (II₄)

42 %. ¹H NMR, δ ppm: 1.60 (quint, *J* = 7.2 Hz, 2H), 1.85 (quint, *J* = 7.2 Hz, 2H), 2.32 (t, *J* = 7.2 Hz, 2H), 3.20 (t, *J* = 6.9 Hz, 2H), 4.11 (s, 4H), 4.15 (s, 5H). ¹³C NMR, δ

ppm: 6.99, 28.51, 31.82, 33.24, 67.53, 68.40, 68.95, 83.47. Anal. calcd. for C₁₄H₁₇FeI: C, 45.69, H, 4.66 %. Found: C, 45.73 %, H, 4.67 %.

2.1.2 6-Iodoethylferrocene, Fc(CH₂)₆I, (II₆)

47 %. ¹H NMR, δ ppm: 1.60 (m, 6H), 1.99 (quint, *J* = 7.5 Hz, 2H), 2.42 (t, *J* = 6.9 Hz, 2H), 3.19 (t, *J* = 6.9 Hz, 2H), 4.10 (d, 4H), 4.14 (s, 5H). ¹³C NMR, δ ppm: 6.99, 28.32, 28.97, 30.22, 31.04, 34.62, 67.57, 68.37, 68.80, 86.73. Anal. calcd. for C₁₆H₂₁FeI: C, 48.52, H, 5.34 %. Found: C, 48.56, H, 5.37 %.

2.1.3 10-Iododecylferrocene, Fc(CH₂)₁₀I, (II₁₀)

36 %. ¹H NMR, δ ppm: 1.22 (br. s, 10H), 1.44–1.33 (m, 4H), 1.79 (quint, *J* = 6.9 Hz, 2H), 2.26 (t, *J* = 6.9 Hz, 2H), 3.19 (t, *J* = 7.2 Hz, 2H), 3.97 (dd, *J*₁ = 4.5 Hz, *J*₂ = 1.5 Hz, 4H), 4.02 (s, 5H). ¹³C NMR, δ ppm: 7.04, 28.16, 28.82, 29.41, 29.45, 29.51, 29.62, 31.12, 32.82, 34.07, 66.96, 68.02, 68.42, 86.78. Anal. calcd. for C₂₀H₂₉FeI: C, 53.12, H, 6.46 %. Found: C, 53.16, H, 6.42 %.

2.1.4 12-Iododecylferrocene, Fc(CH₂)₁₂I, (II₁₂)

30 %. ¹H NMR, δ ppm: 1.26 (br. s, 12H), 1.36 (m, 4H), 1.80 (quint, *J* = 6.9 Hz, 2H), 2.24 (t, *J* = 7.2 Hz, 2H), 3.19 (t, *J* = 7.2 Hz, 2H), 3.97 (dd, *J*₁ = 4.5 Hz, *J*₂ = 1.5 Hz, 4H), 4.00 (s, 5H). ¹³C NMR, δ ppm: 7.02, 28.46, 28.97, 29.49, 29.54, 29.57, 29.62, 29.64, 30.51, 31.33, 33.69, 66.95, 67.47, 68.57, 86.84. Anal. calcd. for C₂₂H₃₃FeI: C, 55.25, H, 6.53 %. Found: C, 55.23, H, 6.54 %.

2.1.5 1,1'-Di(4-iodobutyl)ferrocene, Fc(C₄H₈I)₂, (III₄)

31 %. ¹H NMR, δ ppm: 1.62 (quint, *J* = 7.5 Hz, 4H), 1.85 (quint, *J* = 6.9 Hz, 4H), 2.34 (t, *J* = 7.8 Hz, 4H), 3.16 (t, *J* = 6.9 Hz, 4H), 4.08 (s, 8H). ¹³C NMR, δ ppm: 7.08, 28.34, 32.02, 33.18, 67.01, 67.88, 68.09, 68.50, 68.64, 88.45. Anal. calcd. for C₁₈H₂₄FeI₂: C, 39.31, H, 4.40 %. Found: C, 39.27 %, H, 4.42 %.

2.1.6 1,1'-Di(6-iodohexyl)ferrocene, Fc(C₆H₁₂I)₂, (III₆)

34 %. ¹H NMR, δ ppm: 1.48 (m, 6H), 1.78 (quint, *J* = 7.5 Hz, 4H), 1.99 (quint, *J* = 7.5 Hz, 4H), 2.44 (t, *J* = 6.9 Hz, 4H), 3.20 (t, *J* = 6.75 Hz, 4H), 3.99 (s, 8H). ¹³C NMR, δ ppm: 7.18, 28.77, 29.30, 30.29, 32.55, 34.71, 67.57, 68.6, 87.03. Anal. calcd. for C₂₂H₃₂FeI₂: C, 43.59, H, 5.32 %. Found: C, 43.57, H, 5.34 %.

2.1.7 1,1'-Di(10-iododecyl)ferrocene, $\text{Fc}(\text{C}_{10}\text{H}_{20}\text{I})_2$, (III_{10})

28 %. ^1H NMR, δ ppm: 1.28 (br. s, 20H), 1.35 (m, 4H), 1.46 (m, 4H), 1.82 (quint, $J = 6.9$ Hz, 4H), 2.24 (t, $J = 7.2$ Hz, 4H), 3.19 (t, $J = 7.2$ Hz, 4H), 4.05 (br. s, 8H). ^{13}C NMR, δ ppm: 6.98, 28.14, 28.75, 29.42, 29.48, 29.60, 31.29, 32.81, 34.07, 66.93, 67.61, 68.59, 89.33. Anal. calcd. for $\text{C}_{30}\text{H}_{48}\text{FeI}_2$: C, 50.16, H, 6.73 %. Found: C, 43.57, H, 5.34 %.

2.1.8 1,1'-Di(12-iododecyl)ferrocene, $\text{Fc}(\text{C}_{12}\text{H}_{24}\text{I})_2$, (III_{12})

33 %. ^1H NMR, δ ppm: 1.27 (br. s, 28H), 1.38 (m, 4H), 1.48 (m, 4H), 1.82 (quint, $J = 6.9$ Hz, 4H), 2.29 (t, $J = 7.2$ Hz, 4H), 3.19 (t, $J = 7.2$ Hz, 4H), 3.96 (br. s, 8H). ^{13}C NMR, δ ppm: 7.39, 28.54, 29.41, 29.52, 29.54, 29.59, 29.60, 29.62, 29.65, 30.50, 31.29, 33.55, 67.61, 68.59, 89.38. Anal. calcd. for $\text{C}_{34}\text{H}_{56}\text{FeI}_2$: C, 52.73, H, 7.29 %. Found: C, 52.70, H, 7.27 %.

2.2 Solvents and electrolytes

In this study, voltammetric results were obtained using electrolytic solutions of tetra-*n*-butylammonium tetrafluoroborate (TBABF₄) in acetonitrile (ACN) and *N,N*-dimethylformamide (DMF). All these chemicals were obtained from Aldrich and used without further purification. Supporting salt concentration was in all cases fixed at 0.1 M. Experiments described in this study did not need special treatment of the electrolytic solutions. In particular, there was no special care of getting dry solutions. The average amount of water found in solutions was checked to be about 1,000 ppm.

2.3 Electrochemical procedure

All potentials are referred to the aqueous Ag/AgCl_(sat) reference electrode (with own potential -0.045 V vs SCE at 25 °C) placed in a bridge filled with the corresponding solvent/supporting salt. The electrochemical instrumentation has been previously reported [16]. Electrodes used in voltammetry had an apparent surface area of 0.8 mm^2 . Coulometric measurements and electrolyses described in this report were carried out in three-electrode cells with a total catholyte volume of $5\text{--}7\text{ dm}^3$. A fritted glass separated the anodic compartment. Experiments were completed on small substrate amounts (typically 0.1 dm^3) of RIs. Efficient argon bubbling was completed in all cases in the course of voltammetry and coulometry, enabling good reproducibility of data. Work up consisted of a thorough sonication of the electrodes (during 2 min), then rinsing with acetone before drying them by a hot air stream (60°C).

3 Results

3.1 Reduction of α,ω -diiodoalkanes

Electrochemical reduction of α,ω -diiodoalkanes has been discussed several times in the past [13, 20, 21]. Various electrode materials were used, in particular GC, silver, silver–palladium and copper. As yet, the possibility of covering the electrode surfaces in this process has not been considered. The coverage of carbon surfaces in the course of the cathodic reduction of alkyl halides by primary, secondary and tertiary alkyl groups was only recently revealed. A number of experiments concerning the process of alkylation based on a kind of nucleophilic substitution has been already reported [16–18]. The observation, strongly supporting the alkylation of GC, is the progressive shift of the potential of the two-electron step (which corresponds to the main process resulting in the scission of the carbon-iodine bond) in the course of recurrent scans in voltammetry in aprotic polar solvents. One of the possible arguments explaining those shifts is certainly the progressive coverage of the carbon surface and consequently the slowing down of the first electron transfer reported to need strong activation energy to occur [22]. This feature is also evidenced with α,ω -diiodoalkanes as shown in Fig. 1 for 1,8-diiodooctane as a model substrate. Thus, in the course of the first eight scans (curves shown in A) the $E_{p/2}$ shifts from -1.87 to -2.15 V. These scans, run specifically at the level of the reduction step, exhibit surface coverage [shown by comparing the oxidation of potassium ferrocyanide at a used electrode after these cathodic scans (curves B) and that at a bare GC electrode as shown in D]. Voltammetry of GC electrodes, modified by recurrent scans or by fixed potential electrolyses and then rinsed by sonication in acetone, present a weak reduction step assigned to remnant carbon–iodine bonds. This step totally disappears after one or two scans and this supports the irreversible cleavage of the C–I groups.

At this point, it is necessary to emphasize that the structure of the immobilized organic layer is certainly complex. Several possibilities of surface modification are presented in Scheme 3; their occurrence might depend both on the consumed amount of electricity and on the applied potential. Among numerous possibilities, we can list (A) the presence of a halogenated alkyl end, (B) its hydrogenated form, (C) a bridged form with two anchoring sites and (D–F) similar reactions taking into account polymeric forms via Wurtz-type coupling reactions. It is obvious that only two structures [namely (A) and (F)] are concerned with the additional reduction of remaining C–I bonds. In order to obtain valuable information on the amount of C–I functions still present at the carbon interface, their indirect reduction via redox catalysis was used.

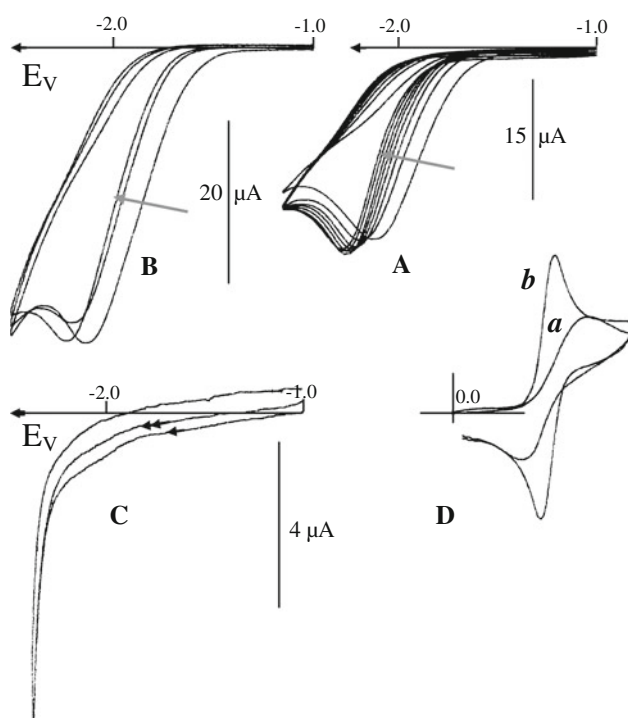


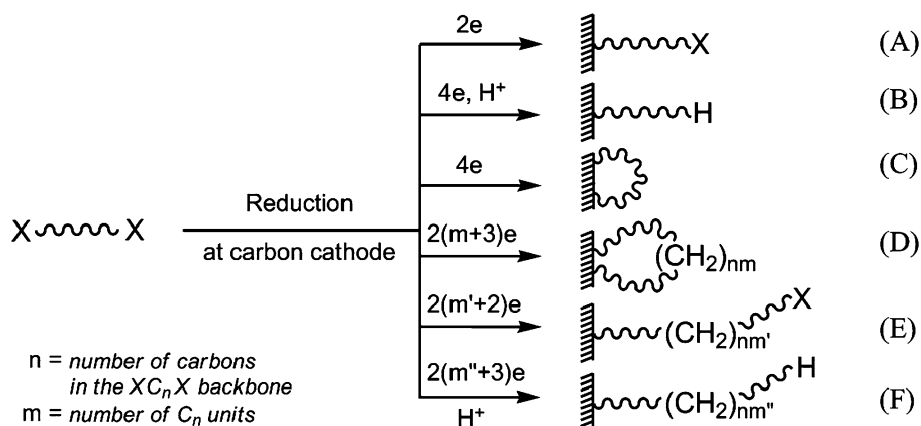
Fig. 1 Cathodic reduction of diiodooctane I_8 (concentration: 8.3 mmol L^{-1}) in DMF + 0.1 M TBABF_4 at GC electrode (surface area: 0.8 mm^2). Scan rate: 0.05 V s^{-1} . **A** Recurrent scans between -1 and -2.6 V . **B** Similar experiment with a I_8 concentration of 12 mmol L^{-1} . **C** Voltammetry of the deposit in a solution free of I_8 after the experiment **B**. **D** Response of potassium ferrocyanide (in saturated KCl solution) at the GC electrode modified under the conditions given in **B**. (a) Modified surface and (b) bare surface after polishing. Cycling between 0 and 0.8 V

Actually, the electrogenerated anion radicals of π acceptors could achieve the indirect reduction of aliphatic iodides and quantify the nature of the surface coverage by coulometry (see Scheme 4). Since its first description and application by Lund [23] back in the 1970s, redox catalysis was amply described and used both for thermodynamic and synthetic purposes [24, 25]. It is noteworthy that, though redox-catalysed reduction by the surface-covering redox polymer was also considered [26], the present case deals with the opposite situation when the redox mediator is in solution and the iodoalkyl substrate is grafted to the electrode surface. This method can efficiently be used to assess the coverage of surfaces by electroactive functionalities through an irreversible cathodic bond scission (examples: C-halogen, C-S and C-N bonds).

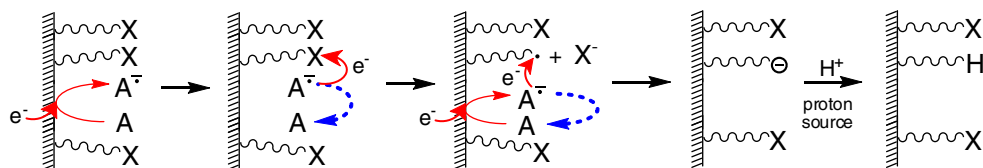
Figure 2 underscores the reduction of C-I bonds by the anion radical of 1-methyl naphthalene by appearance of a pre-peak in (b) meaning that the catalysis is quite certainly fast, but the number of C-I bonds concerned by an indirect electron transfer during the first two scans is presumably quite small.

For comparison, similar experiments using redox catalysis were carried out with the parent bromo-derivatives, like α,ω -dibromoalkanes, which are certainly less electroactive within a comparable potential range. For example, 1,7-dibromoheptane in DMF (with phenanthrene as redox mediator) allowed us to estimate the amount of remnant C-Br bonds at the GC surface as $1.1 \times 10^{-8} \text{ mol cm}^{-2}$ after cathodic reduction of di-halides. Moreover, the case of α -bromo- ω -chloroalkanes was considered because of the foreseen selectivity of the reactive implication of bromine

Scheme 3 Various grafting pathways of diiodo precursors



Scheme 4 Indirect reduction process by means of redox catalysis (A = π acceptor in solution)



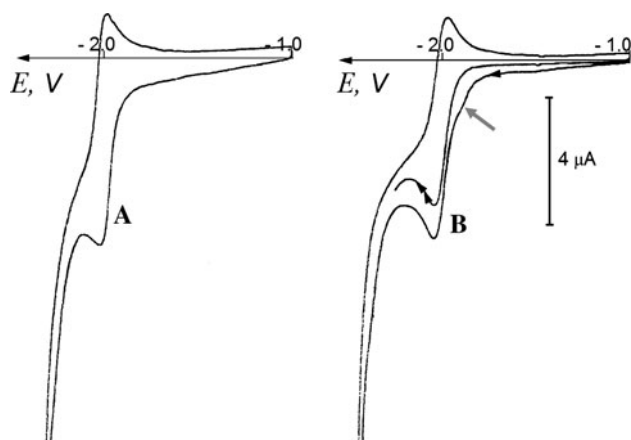


Fig. 2 Iodoalkyl stems deposited onto GC: their indirect reduction by electrogenerated anion radical of 1-methylnaphthalene (1.4 mmol L^{-1}) dissolved in DMF + 0.1 M TBABF_4 . Scan rate: 0.05 V s^{-1} . Reference electrode: Ag/AgCl. **a** Response of methyl-naphthalene alone at a bare GC electrode. **b** Comparative response at the same GC electrode covered using I_8 (see text); first and second scans leading to the total disappearance of the redox reduction of immobilized C–I bonds

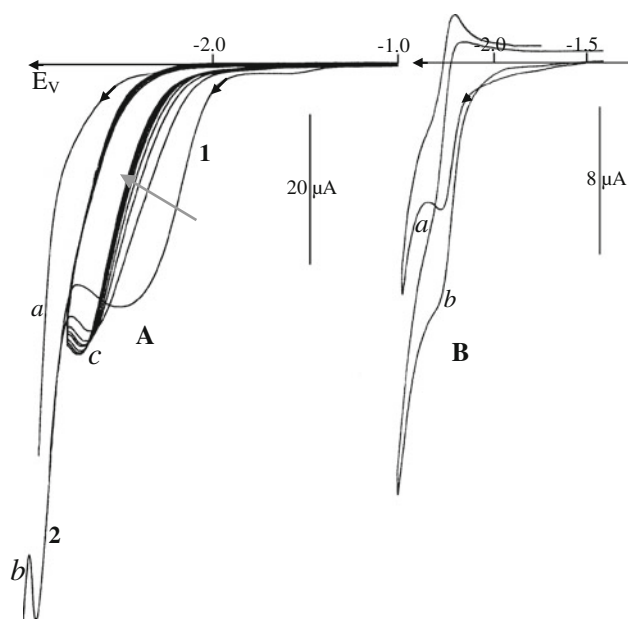


Fig. 3 1-Bromo-4-chlorobutane. Concentration: 16 mmol L^{-1} . Voltammetry in DMF containing TBABF_4 . Scan rate: 0.05 V s^{-1} . GC electrodes (surface area: 0.8 mm^2). **A** One scan (b) between -1.0 and -3.0 V followed by repetitive scans (c) up to -2.8 V . The solvent response is shown in curve (a). **B** Modified electrode during the electrolysis of 1-bromo-4-chlorobutane at -2.2 V (amount of charge passed: $2 \times 10^{-3} \text{ C}$). Cycling in the presence of phenanthrene (3 mmol L^{-1}). Comparison between the voltammetry of phenanthrene alone (a) and that at the modified surface (b), first scans

at the interface. This is displayed in Fig. 3 (large potential difference in voltammetry between the C–Br and the C–Cl bond cleavage starting from -2.17 to -2.85 V ,

respectively) which permitted—with a nice catalytic effect quantified by a large amount of electricity—to deduce that the alkyl-chloro layer is quite certainly prominent at the carbon interface ($\Gamma_{\text{Cl}} = 2.3 \times 10^{-8} \text{ mol cm}^{-2}$). These high coverage values are inherent to the mode of grafting that concomitantly deforms the surface structure leading to a kind of 3D interface. This phenomenon has already been underlined and discussed in a previous report [16]. Note that large amounts of electricity (of the order of several millicoulombs per mm^2 at -2.5 V) during the reaction with α,ω -dihaloalkanes caused severe changes of the structure of GC. In consequence of this, recovering a fresh surface often appeared to be very difficult, so as continuous polishing operations in order to remove several hundreds of microns were quite frequently necessary. Sometimes (when background response was unsatisfactory between -0.9 and -2.5 V), the GC disc deterioration used as the electrode has been noticed.

3.2 Cathodic behaviour of bis-(ω -iodoalkyl)ferrocenes

The experiments described above with diiodoalkanes (I) demonstrated the formation of organic layers onto GC without, however, any possibility of quantifying and providing essential information on the nature of the layer. For that, additional work relative to the attachment of organometallic stems at GC was achieved with ferrocenes (III) and the anodic responses of {Fc} moiety then provided the information on the nature of these layers. For comparison, ω -iodoalkylferrocenes (II) were attached to the surface under the same conditions.

A typical difference between the coverage of GC by mono-iodoferrocenes (II) and di-iodoferrocenes (III) is clearly displayed in Fig. 4 in the case of a short alkyl linkage (butyl chain). By cathodic charge (7 scans) between -1 and -2.6 V , the coverage by ferrocene moieties with (II₄) was found to be $6.0 \times 10^{-9} \text{ mol cm}^{-2}$ while (III₄) gave $9.9 \times 10^{-9} \text{ mol cm}^{-2}$. For (III₄), this value depends on the amount of charge passed and therefore it may vary with the number of scans and the boundaries of potential span. As shown in Fig. 5 (using ACN as solvent instead of DMF under quite similar conditions), after 2 scans and a hold one found a quite similar value, equal to $6.5 \times 10^{-9} \text{ mol cm}^{-2}$. The excess of ferrocene is presumably due to the limited formation of a polymer. The deposit found in DMF would fit roughly with the immobilization of two Fc moieties per site. The attachment to the surface was checked, after careful ultrasonic cleansing, by variation of the scan rate v : the peak currents relative to Fc oxidation were noticed to be almost perfectly proportional to v within the range from 20 to 500 mV s^{-1} . Moreover, anodic and related cathodic potentials were found to be equal at 100 mV s^{-1} (0.50 V),

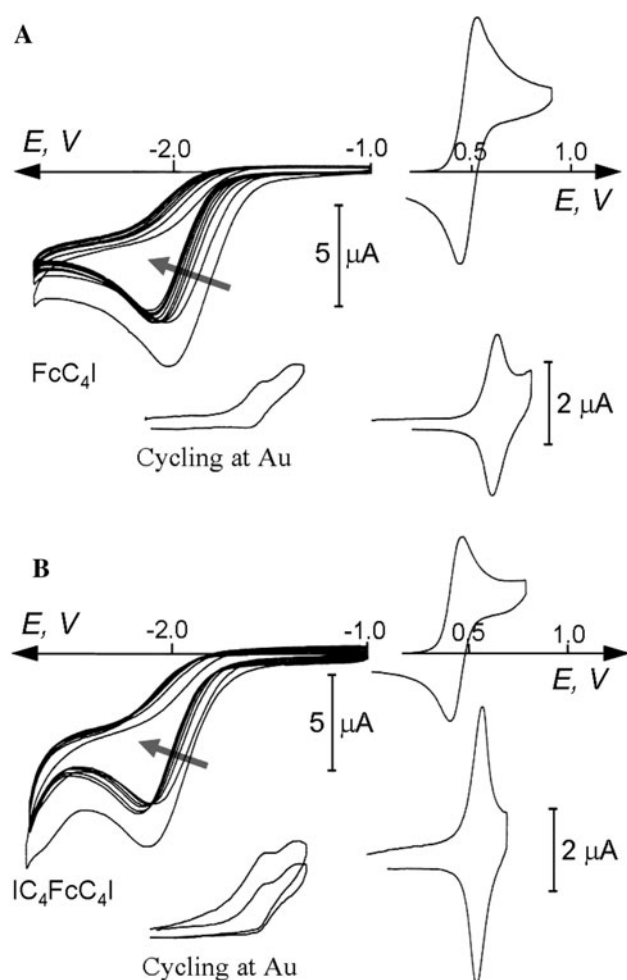


Fig. 4 Comparison between the deposits at the GC electrode. Deposits obtained from **a** moniodo FcC_4I and **b** di(iodobutyl) ferrocene $\text{IC}_4\text{FcC}_4\text{I}$ by cathodic multi-cycling between -1 and -2.7 V. Concentrations of iodoalkylferrocenes in the solution of DMF + 0.1 M TBABF₄ are 7.4 and 4.4 mmol L^{-1} , respectively. Upper right voltammogram at each panel: anodic scan of the corresponding iodoalkylferrocenes in the solution ($\nu = 0.05$ V s^{-1}). Lower row voltammograms: anodic cycling of the modified electrode in the solutions free of ferrocene. Scans between 0 and 0.8 V. For comparison, cycling of deposits at gold electrodes of the same surface area (0.8 mm²) do not display any response assigned to ferrocene

without ohmic correction. The corresponding peak potentials found with (III₄) in solution are 0.51 and 0.44 V. The electronic conductance inside the grafted thin deposited layer thus seems to be high.

With (III₆), the deposited films were found to be thicker and with concomitantly larger amount of immobilized Fc moieties. Fc still displays a lone voltammetric signal but it exhibits some diffusional character for $\nu > 100$ mV s^{-1} . Moreover, the potential slowly increases with ν (from 0.52 V at 20 mV s^{-1} to 0.63 V at 500 mV s^{-1}). The apparent surface concentration also strongly increases up to $\Gamma_{\text{Fc}} = 3.0 \times 10^{-8}$ mol cm^{-2} . This value supports a random increase of immobilization of about 4–5 Fc

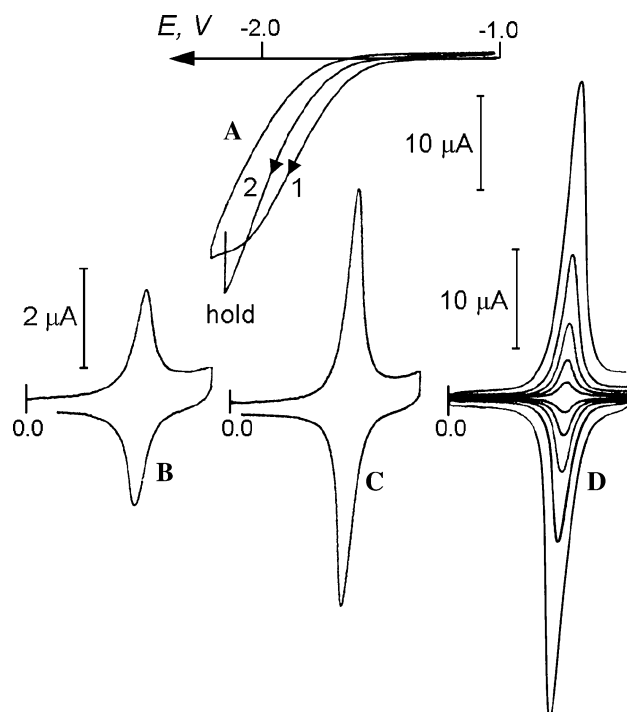


Fig. 5 Electrodeposition of ferrocene via $\text{IC}_4\text{FcC}_4\text{I}$ (concentration: 5.4 mmol L^{-1}) in $\text{CH}_3\text{CN} + 0.1$ M TBABF₄. GC electrode (surface area: 0.8 mm²). Scan rate: 0.05 V s^{-1} . **a** Cathodic reduction: 2 scans + hold during 1 min. **b** Anodic response between 0 and 0.8 V after sonication. **c** Anodic response after 5 scans between -1.0 and -2.6 V. **d** Anodic signals according to **c** at different scan rates ($\nu = 0.02$ – 0.5 V s^{-1})

moieties per site if one compares it to the values obtained with the mono-iodo derivative (II₆).

This tendency is strongly confirmed with much longer alkyl chains (n equal to 10). With (III₁₀), the cathodic step relative to the reduction of the C–I bonds totally vanishes at the eighth scan (Fig. 6). The inhibition of any electron transfer for the layer formed under such conditions is confirmed by the strong decrease of chloranil cathodic peak in DMF at a carbon electrode. Quite surprisingly, at low scan rates (e.g. 50 mV s^{-1}) the anodic response of the film at the first scan is strongly shifted to more positive potentials while it becomes almost perfectly adsorption-like in appearance (peak potentials $E_{\text{p}}^{\text{ox}} = 0.52$ V and $E_{\text{p}}^{\text{red}} = 0.51$ V) during the second scan. However, one may notice that the oxidation peak gains a strong diffusional character (Fig. 7, curve C₁₀). The mean number of Fc moieties per immobilizing site is now around 7. It is expected that the attached polymer changes in structure after the first redox cycle, possibly by swelling because of the incorporation of TBA⁺ cations and solvent molecules.

The solubility of di(iodoalkyl)ferrocenes with longer chains (case of $\text{IC}_{12}\text{FcC}_{12}\text{I}$) in polar electrochemical solvents drops remarkably which possibly makes the SN very slow leading, as corollary, to a weak grafting small surface

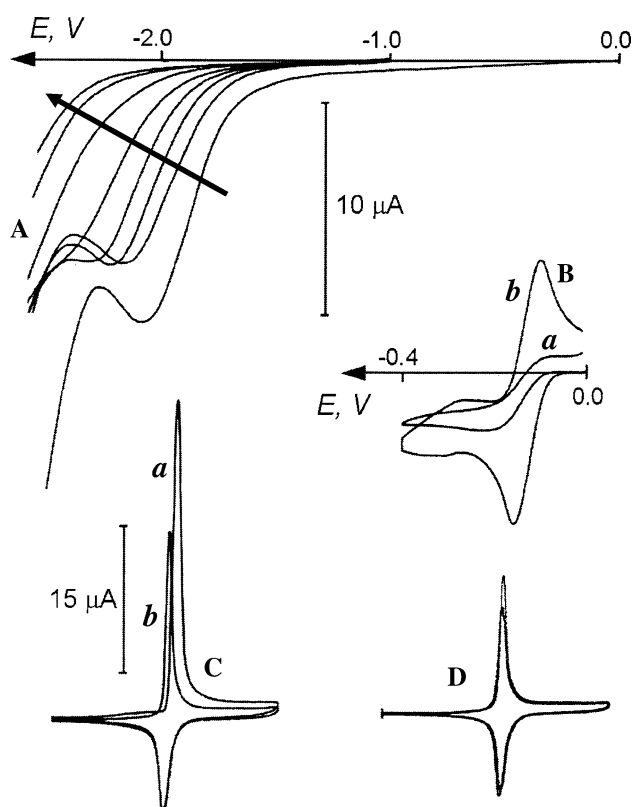


Fig. 6 Voltammetry and immobilization of $\text{IC}_{10}\text{FcC}_{10}\text{I}$ (concentration: 7.2 mmol L^{-1}) at a GC electrode (surface area: 0.8 mm^2). Solvent: DMF containing 0.1 M TBABF_4 . Scan rate: 0.05 V s^{-1} . **A** Recurrent scans up to -2.6 V . Only the forward scans are shown. **B** (a) Response of chloranil (same electrolyte) at the resulting electrode ($v = 0.05 \text{ V s}^{-1}$). For comparison: (b) the same electrode after polishing. **C** Specific response of the surface deposit after 8 scans under the conditions given in **A**. (a) First cycle, (b) second cycle. Cycling between 0 and 1 V . **D** Five following cycles

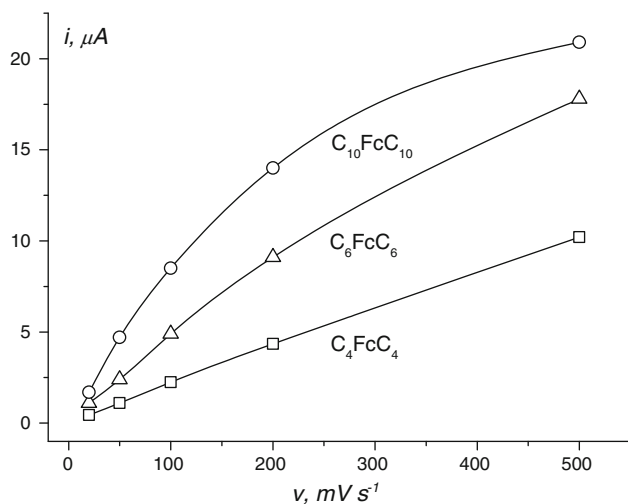


Fig. 7 Anodic peak currents of the grafted C_nFcC_n layers versus scan rate (in DMF + 0.1 M TBABF_4). The corresponding deposits obtained at a GC electrode (areas equal to 0.8 mm^2) after 6 scans between -1.0 and -2.6 V with concentrations of di(iodoalkyl)ferrocenes of about 12 mmol dm^{-3}

coverage. The use of a tetrahydrofuran–DMF (50:50 v/v) mixture did not visibly improve grafting conditions. Concomitantly, electron exchange became much slower as a consequence of hopping between redox sites. The studies concerning mono-iodo FcC_{12}I (with grafting values of Fc quite comparable to other members of the series) confirm, in a certain way, that discrepancies are due to the presence of a polymer.

Electrochemical impedance spectroscopy (EIS) allowed us to assess charge-transfer resistance (R_{CT}) of the layer, freshly grafted onto the GC electrode from $\text{IC}_6\text{FcC}_6\text{I}$ and stabilized by redox cycling (as in Fig. 6c), using ferrocene oxidation as a model redox process (Fig. 8). The initial resistance of the intact layer is quite high, $R_{\text{CT}} \cong 3.5 \text{ M}\Omega$ (which is attributed to the compactness of the redox polymer produced at the interface). The 3D character of GC surface in-depth modification is well seen through the series of Nyquist plots (Fig. 8B) showing that the impedance of a bare GC electrode (Fig. 8C) cannot be simply regained by usual ‘gentle’ polishing of the electrode (Struers 2000 paper); for this, the removal of more than $\approx 100 \mu\text{m}$ —i.e. substantially more than the roughness of the initially polished GC electrode—of the surface material was necessary.

SEM images (Fig. 9) also reveal the bumps growing along the scratches on the GC surface which could possibly be understood as involvement of carbon in the deposition process.

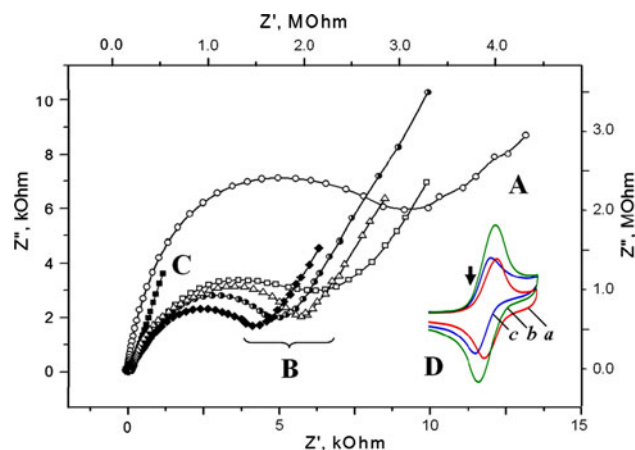


Fig. 8 Nyquist plots for the oxidation of Fc (2.5 mmol L^{-1} in $\text{CH}_3\text{CN} + 0.1 \text{ M Bu}_4\text{NPF}_6$) at a GC electrode modified using $\text{IC}_6\text{FcC}_6\text{I}$ (frequency range from 1 MHz to 0.01 Hz ; $E_{\text{app}} = 0.3 \text{ V}$; $\Delta E = 10 \text{ mV}$): (A) freshly modified electrode (top and right scales). (B) The same electrode after first and several consecutive polishings (left and bottom scales), (C) same (bare) GC electrode after removing the grafted layer. (D) Voltammetry during EIS measurements: (a) freshly modified electrode, (b) same, after addition of Fc, (c) after removal of the grafted layer. Scans from 0 to 0.9 V . The arrow indicates the E_{app}

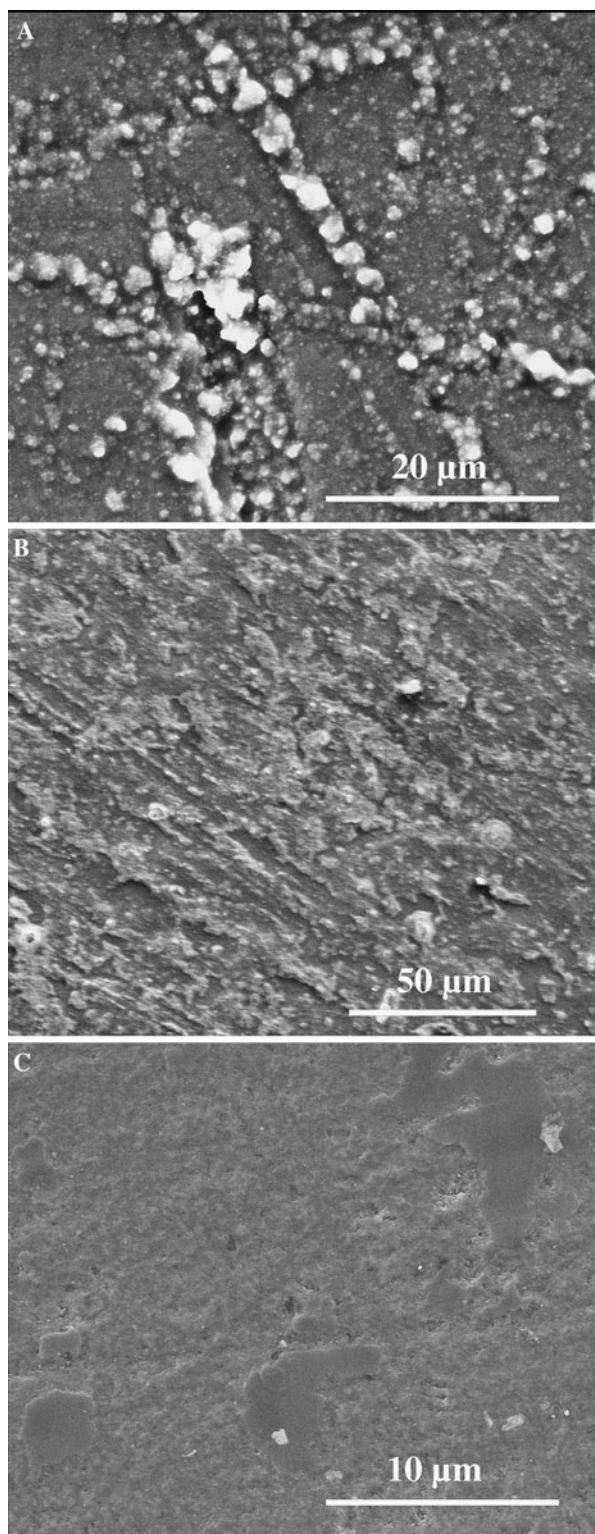
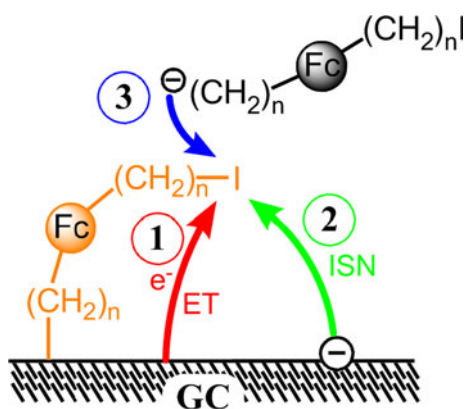


Fig. 9 SEM images of deposits at GC made from $\text{IC}_6\text{FcC}_6\text{I}$ (a) and from $\text{IC}_{10}\text{FcC}_{10}\text{I}$ (b). Electrolyses of 12 mmol dm^{-3} solutions of diiodoalkylferrocenes in AN + 0.1 M TBABF_4 . Applied potential: -2.2 V . Amount of electricity: 2 C cm^{-2} . Samples were sonicated for 2 min and then rinsed with acetone and dried under hot stream at 60°C . For comparison, c shows the aspect of the GC plate surface before the grafting process

4 Conclusion

Cathodic activation of bis(ω -iodoalkyl)ferrocenes at carbon electrodes appears to be an interesting source of new immobilized organometallic redox polymers possessing a certain random distribution of ferrocene moieties in their matrix. Growing this interfacial material occurs apparently in two stages: (i) grafting of a first Fc through an initial electrochemical activation of the carbon surface for creating nucleophilic sites capable of displacing iodine from at least one of the terminal chains of (III_n) species as recently described with (II_n) series [16] followed by (ii) subsequent scission of the second C–I bond with at least three modes of reactivity as sketched in Scheme 5. Path (1) is a simple hydrogenolysis of the C–I bond through the initial electron transfer. The second path (2) may occur from the negatively charged solid surface provided that the alkyl stem is short and the deposited layer is not too thick and bulky. It should correspond to something quite analogous to an S_N substitution. This situation does not appear to occur with monomers III_n with short alkyl chains due to their impeded flexibility, therefore making the double grafting unlikely. The third pathway corresponds to partial heterogeneous two-electron reduction of III_n in solution according to process (3). That corresponds to formation of the carbon–carbon bond by a Wurtz-type reaction which is the key to polymerization and accumulation of immobilized Fc moieties at the polymer–electrolyte interface. We do not expect the number of Fc per grafted chain to be much higher than 7, especially for the species with long alkyl chains ($n = 10$). The as-produced films become too thick to permit fast electron transfer to III_n and this mechanism presumably becomes too slow to occur efficiently. Contrariwise, with short chains (small n values), the direct reduction of the second C–I looks easy and this possibility does not favour such anionic polymerization to a large extent. In summary, the coverage process is controlled by the length of alkyl chains [path (2) vs (3)] that could orientate the ratio between an organic carbanion and a potentially efficient nucleophile for the lengthening of polymer chains. Note also that the prominence of the interfacial nucleophilic substitution (S_NI) pathway has to be dismissed as soon as the carbon surface becomes strongly covered due to a large immobilization of III_n .

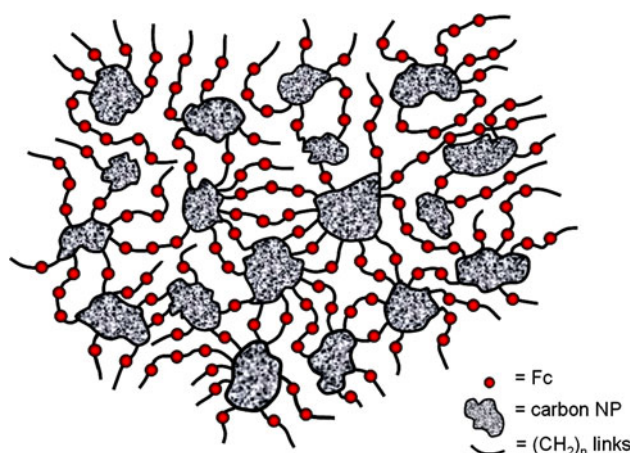
Building of the redox polymer together with side reactions is depicted in Scheme 6, while the charge/discharge process corresponds to that in Scheme 7. Voltammetry of the ferrocene layers, especially shown in Figs. 5 and 6, could correspond to an open polymer well soaked with electrolyte, in which the electron exchanges may happen without large motion of ions at least with moderate lengths of alkyl chains. That such redox systems can be used as interface mediators in indirect oxidation process and



Scheme 5 Three possible pathways of redox polymer formation. 1 Classical heterogeneous electron transfer to the remnant C–I bond. 2 Interfacial nucleophilic substitution after a specific charge of carbon. 3 Homogeneous S_N2 via Wurtz reaction, the chain length conditioning the pathway (if $n \geq 10$, ③ < ② or ①)

electron exchange within such materials has been already considered [26].

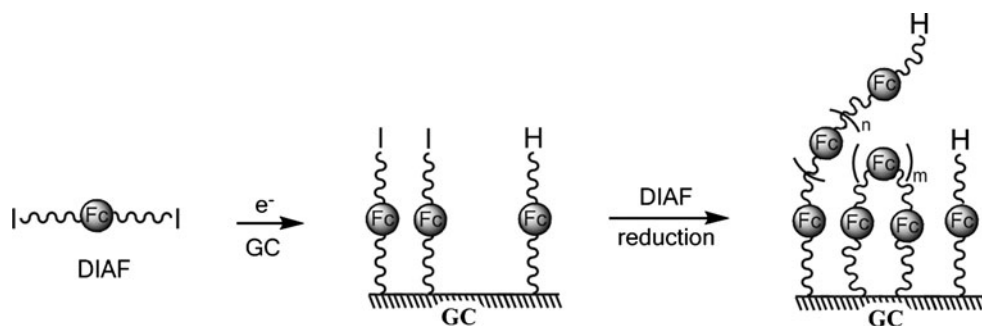
The important feature to underscore the interest of such layers is quite certainly their remarkable ability to enable attachment and/or grafting Fc moieties which permits fast electron transfers during their charge and discharge processes. The bulk polymer/ferrocene/carbon/solvent salt that was tested here appears well conducting although its conductance has not been specifically measured. In fact, several examples described in this article showed that these systems are almost perfectly reversible, quite close to ideal electrochemical character. With these layers so easy to



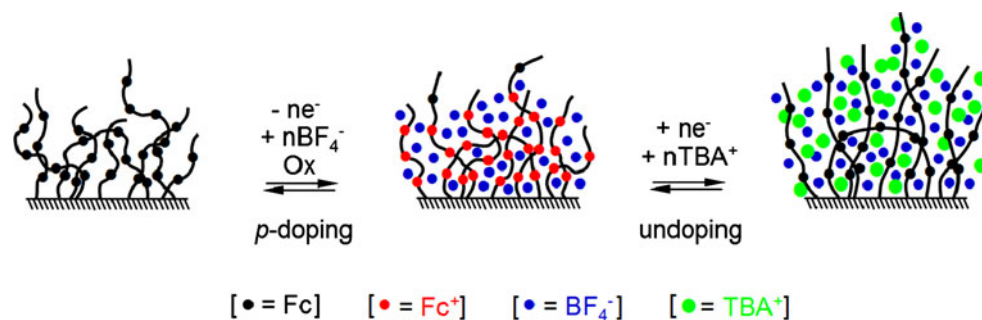
Scheme 8 Carbon nanoparticles linked through electrodeposited alkylferrocenes

build, and taking into account the large extent of immobilization onto simple carbon surfaces (until about 100 times more than expected for perfect and non-modifiable solid surfaces), one may imagine a new electrode material built with taking advantage of all the parameters revealed in this study. A material essentially made of fine carbon powder and simply substituted ferrocene chains could be considered. This material (made of two elements in intimate contact akin to an amalgam) would then permit one to design a practical system (for both the charging and the discharging process) usable to store electricity. In other words, in the presence of extremely fine carbon particles [principally made of graphite and fullerene nanoparticles

Scheme 6 Formation of final alkylferrocene structures at the GC surface



Scheme 7 Immobilization of counter ions in the polymer matrix resulting in its charge and structural modification



(NPs)], associated via redox bridges using IC_nFcC_nI could take place allowing at the same time permeability of this material to electrolyte and solvent. Such a material combining the capacity of certain carbon NPs to store electrons and that of certain organometallic species of high electronic stability to react fast under charge is certainly an attractive idea to test. This perspective [26–28] can be summarized by Scheme 8 where the association of carbon nanoparticles and alkyl ferrocene chains would give an open material allowing electrons to move fast through it in contact with a solvent and a suitable electrolyte. Further study in this direction is underway.

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